DRAFT – FOR DISCUSSION PURPOSES ONLY

Date: January 10, 2008 SOP DUFF-LIBBY-OU3 (Rev. 0)

Title: SAMPLING AND ANALYSIS OF DUFF FOR ASBESTOS

APPROVALS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
EPA Remedial Project Manager	_____ Bonita Lavelle, USEPA RPM	_____
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Revision Number	Date	Reason for Revision
0	01/10/2008	--

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a standardized method for collection and analysis of duff samples for asbestos. Duff, for the purposes of this SOP, is inclusive of partially decayed organic material that occurs on top of soil in forested areas and freshly fallen organic material such as leaves and twigs. This procedure will be used by USEPA Region 8 for the Remedial Investigation work for Operable Unit 3 performed at the Libby Asbestos Superfund site.

Deleted:

Deleted: the layer of loose debris

Comment [DW1]: Here is a possible definition of duff. The "real" definition would not include the freshly fallen material but is something we have included in Phase I. The term duff was never used in the Phase I SAP so we need to abandon the term duff or define it. I believe this was referred to as organic debris.

2.0 RESPONSIBILITIES

The Field Sampling Team Leader is responsible for ensuring that all duff samples are collected in accord with this SOP. The Laboratory Director is responsible for ensuring that duff samples provided to the laboratory for evaluation by this SOP are prepared and analyzed in accord with the requirements of this SOP. It is the responsibility of the Field Sampling Team Leader and the Laboratory Director to communicate the need for any deviations from the SOP with the appropriate USEPA Region 8 Remedial Project Manager or Regional Chemist.

3. 0 EQUIPMENT

3.1 Field Equipment

- Ziploc® plastic bags
- sample identification labels
- GPS unit
- field log book
- field sample data sheet(s)
- ink pen
- clear packaging tape

3.2 Laboratory Equipment /Reagents

- Large aluminum trays
- Drying oven
- Large metal tray(s) (large enough for duff sample to cover bottom up to 1/2 in.)
- Muffle furnace
- Glass stirring rods
- Fume hood
- HEPA filtered hood
- Reagent grade or better acetone
- Reagent grade or better HCl
- Fiber-free deionized (DI) water
- Ultrasonic bath, producing a rate of energy deposition in the range of 0.08-0.12 MW/m^3
- Disposable plastic filter funnel apparatus

- Disposable filter funnels with straight sides [VWR # 145-0020]
- Culture dishes [VWR # 25388-581, case of 500]
- 47 mm 0.45 micron MCE or 0.4 micron PC filters
- Kim wipes or alternative paper
- Ziploc plastic bags
- Glass petri dishes
- Glass microscope slides
- Low temperature plasma asher
- Vacuum evaporator (carbon coater)
- Graphite or carbon rods
- HEPA laminar flow hood
- Acetone vapor generator
- Grids
- Fine forceps
- Grid storage boxes
- Jaffe wick or sponge
- Transmission electron microscope with the following capabilities:
  - 100 Kev
  - fine probe size <250 nm
  - EDXA
  - SAED

4.0 METHOD SUMMARY

A duff sample is collected by hand at a selected area and placed in a plastic bag. Duff samples are prepared for analysis by high temperature ashing to remove organic matter. The residue is then analyzed for LA by transmission electron microscopy (TEM) and/or by Polarized Light Microscopy (PLM), as specified in the project-specific Sampling and Analysis Plan (SAP).

5.0 SAMPLE COLLECTION

[Need input from field team – is this approximately how the duff samples were collected?]

Duff samples should be collected from the soil sampling stations specified in the project-specific SAP. At each specified sampling station, collect any fresh or partially decayed organic debris (e.g., twigs, leaves, pine needles) using a gloved hand from the soil surface within a 6 in. *x* 6 in. area. Care should be taken to ensure that the top layer of soil beneath the organic debris is not included in the duff material sample. Place the duff material into a large, air-tight, re-sealable plastic bag. Label the bag with the same sample identifier as the soil field sample, and place clear packaging tape over the sample identifier label.

Complete the appropriate fields on the soil Field Sample Data Sheet (FSDS) form. Note any special circumstances or conditions about the sampling location. Obtain and record the GPS coordinates of the sampling location on the FSDS form.

6.0 SAMPLE PREPARATION AND ANALYSIS

6.1 Drying and Ashing

Weigh and record the tare weight of a clean, dry aluminum tray of approximately quart size. Fill the aluminum tray to approximately ¾ full. The samples may be split across as many trays as may be needed. Each tray will need to be initially tared and then gravimetrically tracked through the process. Each tray should possess a mark to make it unique and identifiable from the other trays. Place the tray(s) with the sample into a drying oven. Heat to 80°C and hold at this temperature until weight stabilizes (at least 10 hours). Record the dry weight and calculate the mass of the dried duff sample by the difference.

Weigh and record the tare weight of a clean metal tray capable of withstanding the heat of a 450°C oven. Working under a hood, transfer the dried duff to the tared pan(s), place a lid on the pan and move to a muffle furnace. Ramp up the furnace from a cold start to 450°C and hold at this temperature for 18 hours or until all organic matter is removed.

Allow the tray to cool. Remove the lid, weigh and record the mass of the tray(s) plus the ashed residue. Calculate the mass of the ashed residue by difference.

Under a laminar flow hood, slowly pour the ash into a Ziploc bag. If the ash still retains some structure, seal the bag tightly and manipulate the ash by hand to reduce it to a fine homogenous powder. Invert the bag 3-4 times to thoroughly mix the ash.

6.2 TEM Analysis

Acid Treatment

Remove a 0.25 g aliquot of ash and place into a crucible. To the ashed residue in the crucible, add just enough de-ionized water (approx 1-2 mL) to cover the surface of the residue. Slowly add concentrated HCl to the wetted ash (approx. 10-20 mL). Typically a visible effervescing is observed. Add the HCl slowly to keep this reaction controlled. A small glass stirring rod is useful at this point to gently stir the ash and expose all material to the acid.

If after 3-5 minutes there is no further visible reaction, proceed to the next step. If bubbling is still occurring, continue observation and gentle stirring for up to an additional 5 minutes.

Dilute the sample by adding fiber-free DI water directly to the crucible (approx 20 mL) using a squirt bottle. Pour the sample into an unused disposable 100 mL specimen container with lid. Rinse out any remaining residue from the crucible into the specimen container. Do not exceed 100 mL total volume. Bring the total volume to 100 ml with DI water.

Cap the specimen cup and agitate the sample by inversion 5 or 6 times. Loosen the cap slightly and sonicate for 2 minutes. After sonication, tighten the cap and then dry the exterior of the specimen container with kim wipe or equivalent.

Filtration

Agitate the sample by inversion 5 or 6 times. Withdraw an initial aliquot of 0.1 to 1 mL of sonicated sample. Transfer this aliquot into a new disposable specimen container with lid. Bring the volume up to approximately 100 mL with FDI water. [EMSL: Is the FDI water in this step different than the fiber-free DI water used in previous steps?] Cap and agitate by inversion (5 or 6 times).

Filter this entire volume onto a 47 mm mixed cellulose ester (MCE) filter with 0.4 um pore size.

If the filter appears overloaded (overall particulate level > 20%), repeat the process above, selecting a smaller aliquot volume, as suggested by the degree of overloading. Conversely, if the filter looks too lightly loaded, filter a larger aliquot.

After filtration, transfer the filter membranes to individual disposable labeled Petri dishes with lids. With Petri dish covers ajar, gently air dry the filters in a HEPA protected environment.

TEM Examination

Prepare 3 grids for TEM analysis as detailed in International Organization for Standardization (ISO) TEM method 10312, also known as ISO 10312:1995(E). Utilize 2 grids for analysis, and archive 1 grid.

Counting rules

Examine the grids using TEM in accord with ISO 10312 and all relevant Libby site-specific modifications, including the most recent version of LB-000016, LB-000019, LB-000028, LB-000029, LB-000029a, LB-000030, LB-000053, and LB-000066. All fibrous amphibole structures that have appropriate Selective Area Electron Diffraction (SAED) patterns and Energy Dispersive X-Ray Analysis (EDXA) spectra, and having length greater than or equal to 0.5 um and an aspect ratio (length: width) ≥ 3:1, will be recorded on the Libby site-specific laboratory bench sheets and electronic data deliverable (EDD) spreadsheet for TEM analysis of duff samples. Data recording for chrysotile (if observed) is not required.

Stopping rules

The target analytical sensitivity for sample analysis should be specified in the SAP. In the absence of a project-specific target sensitivity, the default sensitivity should be 1E+07 $(\text{grams})^{-1}$, which is likely to correspond to a mass fraction of less than 0.005 grams asbestos per gram duff (dry wt). The analytical sensitivity is calculated using the following equation:

$$S = \frac{EFA}{GO \cdot Ago \cdot Mass \cdot F}$$

where:

EFA = Effective filter area (mm^2)
GO = Number of grid openings counted

Ago	=	Area of one grid opening (mm^2)
Mass	=	Mass of the dried (but not ashed) duff sample (g)
F	=	Fraction of the starting duff sample applied to the filter

Count the sample until one of the following occurs:

- The target sensitivity is achieved.
- A total of 50 or more LA structures are observed. In this case, counting may cease after completion of the grid opening that contains the 50th LA structure.
- A total of 100 grid openings are counted without reaching the target sensitivity or observing 50 LA structures. In this event, the laboratory should contact EPA asking for direction.

Comment [DW2]: Please clarify if this is 50 structures for each grid or 50 total. Mary probably should weigh in here. Clarification may be better served elsewhere..?

TEM Data Deliverable

All data on the number, type and size of LA fibers observed during TEM analysis in the laboratory will be provided as an electronic data deliverable (EDD) using the most recent version of the spreadsheet developed for this purpose ("TEM Duff.xls"). [Spreadsheet currently in development…]

6.3 PLM Analysis

If analysis by PLM is called for in the project-specific SAP, the analysis will be performed on an aliquot of the ashed and homogenized residue using method PLM-VE as detailed in the most recent version of SOP SRC-LIBBY-03. PLM-VE is a semi-quantitative analytical method for asbestos that utilizes Libby-specific reference materials to allow assignment of samples into one of four "bins", as follows:

- Bin A (ND): non-detect
- Bin B1 (Trace): LA detected at levels lower than the 0.2% reference material
- Bin B2 (<1%): LA detected at levels lower than the 1% reference material but higher than the 0.2% reference material
- Bin C: LA detected at levels greater than or equal to 1%

PLM-VE results will be recorded using the most recent version of the the Libby site-specific EDD spreadsheet for PLM-VE analysis ("PLM (VE & PC) Data Sheet and EDD.xls").

7.0 QUALITY ASSURANCE

7.1 Field-Based Quality Assurance

Field Duplicates

Field duplicate duff samples will be collected at a frequency specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%. Each field duplicate should be collected from a location close to the primary sample, and from an area of

approximately equal size. Field duplicate samples should be labeled with a unique identifier. Sample details should be recorded on the appropriate soil FSDS, including the unique identifier of the "parent" field sample.

7.2 Laboratory-Based Quality Assurance for TEM Analyses

Laboratory Blanks

A laboratory blank is a filter that is prepared by processing a clean crucible in the same way that a duff sample is prepared. That is, a clean crucible is treated by addition of DI water and HCl, as described above. The contents of the crucible are then rinsed out, diluted to 100 mL, and an aliquot at least as large as the highest volume aliquot for the sample set is removed and used to prepare a filter for TEM examination. This type of blank is intended to indicate if contamination is occurring at any stage of the sample preparation procedure.

Laboratory blanks should be prepared at a rate specified in the project-specific SAP. In the absence of a project-specific specification, laboratory blanks should be prepared at a rate of 3%.

Comment [DW3]: Another point of potential contamination seems to be the drying oven and furnace. Would it be overkill to run a crucible through this process as well?

Filtration Blanks

A filtration blank is a clean filter that is prepared by passing 100 mL of laboratory FDI water through it. The purpose of this type of blank is to ensure that the filters are not contaminated in the laboratory, and that fluids used for diluting and processing samples are fiber-free.

Filtration blanks should be prepared at a rate specified in the project-specific SAP. In the absence of a project-specific specification, filtration blanks should be prepared at a rate of 2%.

Laboratory Duplicates

Laboratory duplicates will be prepared by applying a second aliquot of ashed residue suspension to a new filter, which is then prepared and analyzed in the same fashion as the original filter. The frequency of laboratory duplicates should be specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%.

Recounts

The precision of TEM sample results should be evaluated by recounting selected grid openings in accord with the requirements specified in the most recent version of LB-000029.

7.3 Laboratory-Based Quality Assurance for PLM-VE Analyses

Laboratory Duplicates

Laboratory duplicate PLM-VE analyses will be prepared by examining a second aliquot of ashed and homogenized residue. The frequency of laboratory duplicates should be specified in the project-specific SAP. In the absence of such specification, the rate should be no less than 5%.

8.0 REFERENCES

International Organization for Standardization. 1995. Ambient Air – Determination of asbestos fibres – Direct-transfer transmission electron microscopy method. ISO 10312:1995(E).

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